WASHINGTON UNIVERSITY

Departments of Physics and Chemistry

St. Louis 5, Missouri

TECHNICAL REPORT No.

5. SPIN RELAXATION IN FREE RADICAL SOLUTIONS EXHIBITING HYPERFINE STRUCTURE — J. P. Lloyd, G. E. Pake

September 25, 1953

CONTRACT N6 ONR-202, TASK ORDER 05
(Paramagnetic Resonance)

with

OFFICE OF NAVAL RESEARCH
U. S. NAVY DEPARTMENT
RDB No. NR 310-802

SPIN RELAXATION IN FREE RADICAL SOLUTIONS EXHIBITING HYPERFINE STRUCTURE*

J. P. Lloyd and G. E. Pake;

Department of Physics
Washington University
Saint Louis 5, Missouri

*Assisted by the joint program of the ONR and the AEC.

1. Introduction

The paramagnetic resonance of the peroxylamine disulfonate ion, $ON(SO_3)_2^{--}$, even in crystals of the potassium salt, is not characterized by the pronounced exchange narrowing frequently observed for free radical molecules. It is perhaps attributable to this weakness of the exchange interaction that one can observe a well-resolved hyperfine splitting from the N^{14} nucleus in liquid solutions containing this ion in concentrations even larger than 0.1 molar.[1] There is, therefore, a range of concentrations over

1. Pake, Townsend, and Weissman, Phys. Rev. 85, 682 (1952).

which magnetic dipole transitions of the coupled system, electronic moment plus nuclear moment, can be observed in fields near 10 gauss with adequate signal-to-noise. Measurements by Townsend[2] have

2. Townsend, Weissman, and Pake, Phys. Rev. 89, 606 (1953).

shown that, in fields up to 50 gauss and at frequencies between 9 and 120 Mc/sec, the Breit-Rabi energy levels for a system with $I = 1$, $J = 1/2$ apply to the peroxylamine disulfonate ion in solution.

The present work concerns itself with the mechanism which maintains the population differential between a particular pair of levels participating in resonance absorption. This mechanism will also be shown in the system at hand to dominate in producing the observed line width. The mechanisms of interest in determining measured widths of paramagnetic resonances are, in general, the spin-spin and spin-lattice interactions, which may occasionally be

markedly obscured by instrumental effects. The advantages of working in low fields (~30 gauss) are two-fold. First, the individual hyperfine components become only a fraction of a gauss wide at concentrations below about 10^{-2} molar. In the magnetic fields of several thousand gauss, which correspond to microwave frequencies, care must be exercised to assure that field inhomogeneities over the sample do not contribute to the measured line width. If, for example, Helmholz coils or a solenoid are used in producing the 30 gauss field, no effort at all is required to keep inhomogeneities below 10^{-2} gauss over a sample of several cubic centimeters volume. The second advantage is more compelling. To separate non-negligible spin-spin processes, if any, from the spin-lattice interactions limiting the lifetime of a spin-state, one needs to know the spin-lattice relaxation time. While this can be measured with difficulty at microwave frequencies[3,4], microwave generators with adequate

3. C. P. Slichter, Thesis, Harvard University. Also Phys. Rev. 76, 466 (1949).
4. Schneider and England, Physica 17, 221 (1951).

power are not presently available in this laboratory, and the techniques, in any event, are not as easily applied as those using lumped parameter circuits.

The Hamiltonian function describing the interaction leading to the hyperfine structure is[5]

$$\mathcal{H} = g_J \mu_0 H_0 J_{Z_{op}} + a\, \vec{I} \cdot \vec{J} - g_I \mu_0 H_0 I_{Z_{op}} \qquad (1.01)$$

5. G. Breit and I. I. Rabi, Phys. Rev. 38, 2082 (1931). See also Nafe and Nelson, Phys. Rev. 73, 718 (1948).

where g_J is the spectroscopic splitting factor for the free radical; for a free electron $g_J = g_e = 2.0023$. The magnitude of the Bohr magneton is μ_o, and the antiparallellity of J and the magnetic moment of the electron is explicitly taken into account by the positive sign preceding the first term of (1.01). H_o is the applied external field, and a is the hyperfine coupling constant. Since we take g_I as the nuclear g factor referred to the (positive) Bohr magneton, μ_o, it is the conventional nuclear g divided by $M/m = 1836$.

The Breit-Rabi energy levels[5] given by the Hamiltonian (1.01) for $I = 1$, $J = 1/2$ are displayed in Fig. 1. It is perhaps worthwhile to point out that, for a free radical molecule, one does not know in advance the sign of the hyperfine coupling constant a since the molecular orbitals for the ground state are an unknown superposition of atomic orbitals which may include those correspon- ding to atomic s or p states. The former contributes to a through the electron probability density at the nucleus, whereas p states contribute a term of opposite sign involving the average value of r^3 over the orbit. Even if a particular symmetry operation leads to the molecular counterpart of parity as a good quantum number, in such a way that molecular Σ and π states cannot be superimposed, one does not know without additional spectroscopic studies whether the ground state of $ON(SO_3)_2^{--}$ is even or odd with respect to this quantum number, and the sign of a remains unknown.

This ambiguity of sign means that Fig. 1 may be incorrect, and should perhaps be reflected in the abscissa axis. It is also impossible, therefore, to know which branch of levels will have a

crossover point at fields sufficient to decouple the nucleus from the electron (although the sign of the nuclear g-factor fixes the position of the levels after the crossover). For our work in oscillating rf fields, at frequencies even as high as 10,000 Mc/sec, the ambiguity of sign has no effect on the transition frequencies, since the spacing between the levels is, of course, unaltered by reflecting the energy level scheme. A rotating field could be used to settle the question of the sign of a if it were desired.

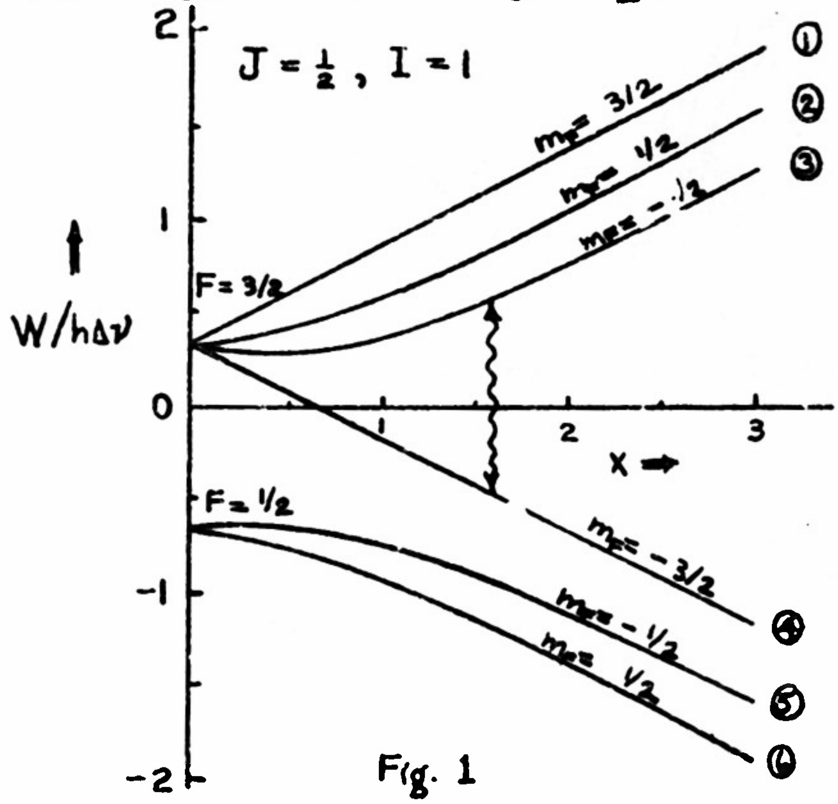


Fig. 1

The particular transition studied in the present work is that between the levels $F = 3/2$, $m_F = -1/2$ and $F = 3/2$, $m_F = -3/2$. This transition has a frequency which increases monotonically from zero. However, the ratio of frequency-to-field is not effectively constant until large enough fields are attained to decouple J from I. In order to treat the spin interaction processes later on, we reproduce here the wave functions and energies which apply to the

levels involved in the transition marked in Fig. 1. The variable is $x = (g_J - g_I)\mu_0 H_0/h\Delta\nu$; from Townsend's measurements[2], $x = 1$ corresponds to $H_0 = 19.5$ gauss.

Table I

F	m	$\psi(F,m) = \sum_{m_J, m_I} (Fm \mid m_J m_I)\,\phi(m_J)\,\chi(m_I)$
$\frac{3}{2}$	$\frac{3}{2}$	$\psi_1 = \phi(\frac{1}{2})\,\chi(1)$
$\frac{3}{2}$	$\frac{1}{2}$	$\psi_2 = a\,\phi(\frac{1}{2})\,\chi(0) + b\,\phi(-\frac{1}{2})\,\chi(1)$
$\frac{3}{2}$	$-\frac{1}{2}$	$\psi_3 = c\,\phi(\frac{1}{2})\,\chi(-1) + d\,\phi(-\frac{1}{2})\,\chi(0)$
$\frac{3}{2}$	$-\frac{3}{2}$	$\psi_4 = \phi(-\frac{1}{2})\,\chi(-1)$
$\frac{1}{2}$	$-\frac{1}{2}$	$\psi_5 = c\,\phi(-\frac{1}{2})\,\chi(0) - d\,\phi(\frac{1}{2})\,\chi(-1)$
$\frac{1}{2}$	$+\frac{1}{2}$	$\psi_6 = a\,\phi(-\frac{1}{2})\,\chi(1) - b\,\phi(\frac{1}{2})\,\chi(0)$

(1.02)

The coefficients, as functions of $x = (g_J - g_I)\,\mu_0 H_0/h\Delta\nu$, will be expressed in terms of $r = (1 + \frac{2}{3}x + x^2)^{1/2}$ and $\rho = (1 - \frac{2}{3}x + x^2)^{1/2}$.

$$\left.\begin{aligned} a^2 &= \frac{1}{2} + \sqrt{\frac{1}{4} - \frac{2}{9r^2}} \\ b^2 &= \frac{1}{2} - \sqrt{\frac{1}{4} - \frac{2}{9r^2}} \\ c^2 &= \frac{1}{2} + \sqrt{\frac{1}{4} - \frac{2}{9\rho^2}} \\ d^2 &= \frac{1}{2} - \sqrt{\frac{1}{4} - \frac{2}{9\rho^2}} \end{aligned}\right\} \qquad (1.03)$$

The energy levels of Fig. 1 are given by

$$W_{F = I \pm \frac{1}{2}} = -\frac{h\Delta\nu}{6} + g_I\mu_0 H_0 m \pm \frac{h\Delta\nu}{2}\left(1 + \frac{4mx}{3} + x^2\right)^{1/2} \tag{1.04}$$

The experiments to be discussed in Section 8 involve excitation of transitions between levels 3 and 4 of Fig. 1 at a frequency

$$\nu_{43} = \Delta\nu\left\{-\tfrac{1}{2}(1-x) + \tfrac{1}{2}\left(1 - \tfrac{2}{3}x + x^2\right)^{1/2}\right\} + g_I\mu_0 H_0/h \tag{1.05}$$

of 60 Mc/sec, which corresponds to an external magnetic field of about 31.4 oersteds. Values of the coefficients of Eqs.(1.03) for this field are listed below:

$$\left.\begin{aligned} a^2 &= 0.950 \\ b^2 &= 0.050 \\ c^2 &= 0.903 \\ d^2 &= 0.097 \end{aligned}\right\} \quad x = g_J\mu_0 H/\Delta\nu = 1.610$$

For the $ON(SO_3)_2^{--}$ ion, $g_I/g_J \approx 10^{-4}$ and we shall usually neglect g_I in comparison with g_J.

2. Paramagnetic Relaxation and Spin Saturation

Paramagnetic relaxation is the process of energy exchange between an assembly of paramagnetic spins and its surroundings which permits the spin-state populations to adjust themselves to the equilibrium distribution corresponding to a given magnetic field and temperature. It is customary to regard the entire paramagnetic sample (solid, liquid, or gas) as a super system composed of two weakly interacting sub-systems; the system of interest or spin system, having spin coordinates among its degrees

of freedom, and the surroundings or lattice system having only orbital degrees of freedom.

It is the weak interaction, $\mathcal{H}_{s\ell}$, between spins and the lattice which is the object of relaxation studies. In practical cases, the question is one of trying to discover which of a number of possibly important spin-lattice interactions effects the experimentally observed relaxation. In certain examples relaxation has been studied experimentally through direct observation of the characteristic time required for the establishment of spin equilibrium (the <u>relaxation time</u>). In other examples, particularly if the relaxation time is short, one measures essentially the thermal conductivity between the spins and the lattice by observing the rate at which energy, absorbed by the spins from a laboratory source, is passed on to the lattice via the relaxation mechanisms; this is the saturation method.

It is of course quite feasible to cloak these measurements in thermodynamic terms, as was done by Casimir and du Pré[6]. We

---

6. Casimir and du Pré, Physica 5, 507 (1938).
   H. B. G. Casimir, Physica 6, 159 (1939).

---

shall usually confine our approach to that of quantum statistics and speak in terms of the transition probabilities per unit time induced by $\mathcal{H}_{s\ell}$. Either a direct relaxation time measurement or a saturation experiment will be treated in terms of the way in which the populations of the various energy states are influenced by these probabilities.

Such an analysis of the relaxation time for an assembly of spin 1/2 particles is straightforward[7]; a unique relaxation time is easily defined for the establishment of the equilibrium population

7. Bloembergen, Purcell, and Pound, Phys. Rev. 73, 679 (1948); often referred to hereafter as BPP.

difference between the two spin-states accessible to each particle. However, a more complicated energy level scheme may not permit the association of a single relaxation time with each pair of levels between which a population difference will exist at equilibrium. An example is the coupled system consisting of the odd electron and the N^{14} nucleus of the free-radical ion $ON(SO_3)_2^{--}$. Not only are there six unevenly spaced levels, but the selection rules permit magnetic dipole transitions between all but five of the fifteen different pairs of levels. In general, one finds that the approach, from an initially disturbed state, to the equilibrium level population is described by an expression of the form

$$N_k(t) = \sum_l b_{lk} \exp(-\lambda_l t) . \qquad (2.01)$$

If after appreciable elapse of time, several comparable terms in the sum (2.01) are dominant, it will be impossible to express any population difference, involving level k, with only one exponential term, and there will be no single relaxation time.

The saturation procedure does not suppose any specific mathematical form for the approach to equilibrium of the population difference between a pair of levels. This method excites transitions between the levels in question by means of a laboratory radiation

field. (We presume throughout this discussion the existence of a constant external magnetic field which removes the orientation degeneracy of individual spins). As we shall later verify (sec 4), the transition probabilities induced by the laboratory field are, for practical purposes, microscopically reversible, which means that the net energy absorption -- and therefore also the detected rf absorption signal -- is proportional to the population difference. In the presence of a given laboratory radiation field, then, a stationary spin population distribution will ultimately obtain in which this rf absorption is just balanced by the energy carried to the lattice through all relaxation processes. (As taken up in section 5 the transition probabilities describing the relaxation processes <u>cannot</u> possess microscopic reversibility if there is to be a non-vanishing population differential at equilibrium.) It follows that a study of relative absorption intensity as a function of the rf power level must give direct information about the interaction $\mathcal{H}_{s\ell}$ which permits energy exchange between the spins and the lattice.

Explicit emphasis should perhaps be given to the fact that a given level of saturation is characterized by <u>stationarity</u> of spin population, but not, of course, by thermal equilibrium. Indeed, the stationarity exists only if the thermal capacity of the lattice, which is in turn normally in excellent thermal contact with its laboratory surroundings, is large. Except at very low temperatures, this condition is usually fulfilled. For this reason, although there is a steady flow of energy into the lattice, we shall speak of a lattice temperature, assumed not to change during a given

measurement, which is essentially a temperature fixed by the sample's immediate laboratory surroundings.*

---

* In the early unsuccessful attempt of Gorter to observed nuclear paramagnetic resonance, the small change of lattice temperature during application of a strong rf field at the Larmor frequency was to be the means of detecting the nuclear spin resonance (Physics 3, 995 (1936)).

---

3. Definition of the Saturation Factor and the Relaxation Probability.

The foregoing description of the saturation procedure suggests that a useful quantity in relaxation studies is the ratio

$$S_{jk}(H_1) = \frac{N_k'-N_j'}{N_k-N_j} \tag{3.01}$$

which we shall call the saturation factor. Here N_k is the stationary population of spin state k with zero or negligible rf field present (thus the thermal equilibrium value) and N_k' is the stationary population in the presence of an rf field H_1. Evidently $S_{jk}(0) = 1$ and $S_{jk}(\infty) = 0$. For a given input of rf power at spin resonance, one expects S_{jk} to depend upon lattice temperature and the external field in which resonance occurs.

We now wish to obtain a relationship which expresses the saturation factor in terms of the laboratory-induced transition probability per unit time, V_{jk}, and the transition probability per unit time, U_{jk}, which is induced by the spin-lattice interaction $\mathcal{H}_{sl}$. We shall let $W_{jk} = U_{jk} + V_{jk}$ denote the probability per unit time, due to both relaxation mechanisms and the laboratory apparatus, that a system now in spin state j will be found at a later time in state k.

If there are a total number N of spin systems to be distributed over the n states accessible to an individual spin, then the following differential equations describe the shifting of the population fractions, $Q_j = N_j/N$, by expressing essentially the conservation of systems:

$$\frac{dQ_j}{dt} = \sum_{\substack{k=1 \\ k\neq j}}^{n} (Q_k W_{kj} - Q_j W_{jk}) \quad \left[j=1,\ldots,n\right] \tag{3.02}$$

Under conditions of population stationarity, Eqs.(3.02) become n homogeneous linear equations in the Q's which are readily seen to be consistent, since any row of their coefficient determinant is obtainable by adding the other n-1 rows. The Q's are of course not all independent, since if n-1 of them are known, the $\underline{n}^{th}$ is determined. Thus the system of equations may be solved by replacing any one of the $\underline{n}$ homogeneous equations

$$\sum_{\substack{k=1 \\ k\neq j}}^{n} (Q_k W_{kj} - Q_j W_{jk}) = 0 \qquad \left[j=1,\ldots,n\right] \tag{3.03}$$

by

$$\sum_{k=1}^{n} Q_k = 1 \tag{3.04}$$

To determine the saturation factor S_{qp}, we require the difference $\Delta_{pq} = Q_p - Q_q$ under the conditions

$$\left.\begin{aligned} W_{jk} &= U_{jk} \qquad \left[qp \neq jk \neq pq\right] \\ W_{pq} &= U_{pq} + V \\ W_{qp} &= U_{qp} + V \end{aligned}\right\} \tag{3.05}$$

expressing the reversibility of $V_{pq} = V_{qp} = V$ and that the laboratory source induces transitions between states p and q only.

For simplicity, let us arbitrarily number the states p and q between which the radiation field produces transitions with the probability V, by the numbers 1 and 2. Then, substituting $Q_2 = \Delta_{21} + Q_1$, one obtains the following equations

$$\left.\begin{array}{llllll}
Q_1 \left[U_{21} + V - (V + \sum_k U_{1k})\right] & + \Delta_{21}(U_{21}+V) & + Q_3 U_{31} & + \ldots + & Q_n U_{n1} & = 0 \\
Q_1 \left[U_{12} + V - (V + \sum_k U_{2k})\right] & - \Delta_{21}(V + \sum_k U_{2k}) & + Q_3 U_{32} & + \ldots + & Q_n U_{n2} & = 0 \\
\vdots & \vdots & \vdots & & \vdots & \\
Q_1 \; (U_{1m} + U_{2m}) & + \Delta_{21} U_{2m} & + Q_3 U_{3m} & + \ldots + & Q_n U_{nm} & = 0 \\
\vdots & \vdots & \vdots & & \vdots & \vdots \\
Q_1 \; (U_{1n} + U_{2n}) & + \Delta_{21} U_{2n} & + Q_3 U_{3n} & + \ldots - & Q_n \sum U_{nk} & = 0
\end{array}\right\} \quad (3.06)$$

Noting that V, by virtue of its practical microscopic reversibility, appears only in two positions in the second column, one can eliminate one V term by replacing, for example, the second equation by Eq.(3.04). If one then solves for Δ_{21} by expanding determinants in terms of the cofactors of the second column, he obtains

$$\Delta_{21} = \frac{C_{22}}{\sum_k U_{2k} C_{2k} + V \cdot C_{21} + C_{22}} \qquad (3.07)$$

where C_{2k} is the cofactor of the second column element in the k^{th} row. For a spin system in thermal equilibrium at room temperature, $\Delta_{21} \sim (E_2 - E_1)/kT = h\nu/kT$. For magnetic dipole transitions which would occur at radiofrequencies between 1 MC/sec and 30,000 Mc/sec, Δ_{21} ranges between 10^{-7} and 5×10^{-3}.

Then Eq.(3.07) indicates that $\sum_{k=3} U_{2k} C_{2k}$ exceeds C_{22} by a factor at least 200 (and, for the experiments of Section 7, by 10^5). Hence C_{22} can be dropped from the denominator of Eq.(3.07) and

one finds $S_{12} = \Delta_{21}(V)/\Delta_{21}(0)$ to be

$$S_{12} = \cfrac{1}{1+\cfrac{V}{U_{21} + \frac{1}{C_{21}} \sum_{k=3}^{n} U_{2k}C_{2k}}} \tag{3.08}$$

This may be compared with BPP's Eqs.(1;), (4) and (33) to show that our result reduces to theirs when there are just two levels. Although a system of many levels without special selection rules does not generally admit to definition of a single relaxation time for a pair of levels, the coefficient of V in Eq.(3.08), which for a two level system is twice the relaxation time T_1, is nevertheless the significant quantity indicating the potency of relaxation mechanisms which give rise to the U_{jk} transition probabilities. We shall define the reciprocal of the coefficient of V to be the <u>relaxation probability</u>, W_R:

$$W_R = U_{21} + \frac{1}{C_{21}} \sum_{k=3}^{n} U_{2k}C_{2k} \tag{3.09}$$

We can thus speak of measuring relaxation probabilities in situations where it is not strictly correct to speak of measuring relaxation times.*

---

* To the extent that Bloch's phenomenological equations (Phys. Rev. <u>70</u>, 460 (1946)) adequately represent the motion of the magnetization vector associated with a particular spin system, the time T_1 describing the exponential decay of that magnetization will, of course, be a perfectly useful parameter. However, one cannot assert generally that the Bloch T_1 bears any simple relationship to the λ's of Eq.(2.01).

4. The Laboratory-induced Transition Probability

Experimental measurement of W_R can be made by measuring S for a known rf field and using the result of Eqs.(3.08) and (3.09),

$$S = \left[1 + V/W_R\right]^{-1} , \qquad (4.01)$$

once we know how V depends upon the rf field.

The probability V_{jk} is often calculated from the semi-classical perturbation treatment of radiation,[8] in which event one

---

8. See, for example, L. I. Schiff, Quantum Mechanics (McGraw-Hill Book Co., 1949), sections 29 and 35.

---

assumes the existence of zero order spin functions u_n, which satisfy the eigenvalue equation

$$\mathcal{H}_s u_n = E_n u_n , \qquad (4.02)$$

and a perturbing interaction

$$\mathcal{H}' = A\left[e^{i\omega t} + e^{-i\omega t}\right] = 2A \cos \omega t. \qquad (4.03)$$

In our case of particular interest in magnetic dipole transitions, A may arise from an interaction $-\vec{\mu}\cdot\vec{H}$ where $\vec{H}$ is the field of the oscillator used in the laboratory to cause spin resonance. Then the usual time-dependent perturbation calculation yields the following first order expression for the probability that the system, initially in a state j, will be found in state k.

$$\left|a_k(t)\right|^2 = \hbar^{-2} \left|(k|A|j)\right|^2 \frac{4 \sin^2 \frac{1}{2}(\omega_{kj} - \omega)}{(\omega_{km} - \omega)^2} \qquad (4.04)$$

Now for times not too short,

$$\frac{4\sin^2\frac{1}{2}(\omega_{kj}-\omega)t}{(\omega_{kj}-\omega)^2} = t\,\delta(\nu_{kj}-\nu), \tag{4.05}$$

and the probability per unit time is

$$V_{j\to k} = \hbar^{-2}\,|(k|A|j)|^2\;\delta(\nu_{kj}-\nu) \tag{4.06}$$

If we take $\mathcal{H}' = -\mu_x(2H_1)\cos\omega t$ and suppose that the spin resonance frequencies of the individual spins of the sample are distributed over a finite frequency range according to a normalized line shape function $g(\nu)$, then

$$V_{jk} = \hbar^{-2}\,H_1^2\;|(k|\mu_x|j)|^2\;\;g(\nu). \tag{4.07}$$

The V_{jk} so obtained is of necessity microscopically reversible, because μ_x is Hermitian.

If, however, the quantum nature of the radiation field is taken into account, the probability of absorptive transition is proportional to the mean number of photons $n(\nu)$ per degree of freedom of the field coordinates belonging to waves of frequency ν. If $\rho(\nu)d\nu$ is the energy density of the field per unit volume in the frequency range $d\nu$, then[9]

$$n(\nu) = \frac{c^3}{8\pi h\nu^3}\;\rho(\nu) \tag{4.08}$$

---

9. Condon and Shortley, Theory of Atomic Spectra (Cambridge University Press, 1935) 80.

The quantum treatment of emission shows it to be proportional to $n(\nu) + 1$, thus including in the theory the spontaneous emission probability (when $n(\nu) = 0$) arrived at by Einstein from statistical considerations of thermal equilibrium. To test the effective reversibility of emission and absorption probabilities, we evaluate $(n(\nu)+1)/n(\nu)$ for the signal generator, assuming it to produce an rf field of about 0.1 gauss in a frequency interval of at most 100 cycles/sec in 6×10^7 cycles/sec. One finds from Eq.(4.08) that $n(\nu)$ is at least 10^{25}. Then clearly, to the extent that $n(\nu)+1 \cong n(\nu)$, we may consider that $V_{jk} = V_{kj}$ even when the quantum nature of our laboratory radiation field is taken into account. We shall use for either V_{jk} or V_{kj} the semiclassical result (4.07), which, since it is proportional to $H_1{}^2$ and includes no possibility of spontaneous emission, must correspond in principle to the actual absorption probability.

5. The Transition Probabilities Effecting Relaxation.

The application of perturbation theory to the calculation of transitions induced by $\mathcal{H}_{s\ell}$ is, in principle, straightforward. One treats $\mathcal{H}_{s\ell}$ as a perturbing interaction for the zero-order Hamiltonian

$$\mathcal{H}_0 = \mathcal{H}_s + \mathcal{H}_\ell \tag{5.01}$$

where $\mathcal{H}_s$ and $\mathcal{H}_\ell$ are respectively the spin and lattice Hamiltonians. In practice, however, even the assembly of spins, which may often be considered as non-interacting among themselves, offers a highly degenerate system for which the orthonormal zero-order linear combinations are not known, and the normal for the lattice are not known

either. The classic example of a serious effort to take into account the normal modes for a particular lattice is Van Vleck's momumental calculation of the relaxation times for titanium and chrome alums.[10]

10. J. H. Van Vleck, Phys. Rev. 57, 426 (1940).

Our experiments deal with liquids, for which there is available almost no information on "lattice" eigenstates. Bloembergen, Purcell, and Pound[7] have, however, obtained excellent results for nuclear paramagnetic relaxation in liquids by approaching the problem from the point of view of the correlation spectrum. The procedure is effectively one of using the semi-classical perturbation treatment for the effect of an oscillatory magnetic field component which might arise through translational or rotational motions of the charges associated with molecules of the liquid; these frequency components are then taken to be distributed according to the correlation spectrum. We can illustrate this procedure by taking A of our Eq.(4.06) as a product*, one factor containing

*or as a sum of such product terms.

(lattice) space coordinates and the other dependent upon angular momentum operators:

$$A = f(r)\, F_{op}(I,J) \tag{5.02}$$

Then Eq.(4.06) becomes

$$U_{j\to k} = \hbar^{-2} |f(\vec{r})|^2 |(k|F_{op}|j)|^2\, \delta(\nu_{kj} - \nu) \tag{5.03}$$

The correlation theory for liquids leads to the conclusion that $|f(r)|^2$ is distributed spectrally according to the intensity

$$J(\nu) = \langle |f(\vec{r})|^2 \rangle_{av} \frac{2\tau_c}{1 + 4\pi^2 \nu^2 \tau_c^2} \tag{5.04}$$

where τ_c is the correlation time and the average is over all time or, equivalently, over all space if $f(\vec{r})$ is a function of coordinates which vary randomly with time. Combining Eqs.(5.03) and (5.04),

$$U_{jk} = \hbar^{-2} \langle |(k|f(\vec{r})\ F_{op}(I,J)\,|j)|^2 \rangle_{av} j(\nu_{kj}) \tag{5.05}$$

where $j(\nu)$ is the normalized spectrum

$$j(\nu) = \frac{2\tau_c}{1 + 4\pi^2\nu^2\tau_c^2} . \tag{5.06}$$

We now ask to what extent a proper quantum approach, analogous to Van Vleck's for the alums, would yield significant features not present in this semi-classical result.

Following the procedure of Sommerfeld and Bethe[11], for example, we would prefer to have quantized the normal modes of the lattice. The lattice states would then be described by a set of

---

11. Somerfeld and Bethe, Handbuch der Physik, 2nd ed., vol. 24/2 (Springer, 1933) 500ff.

---

quantum numbers n_i for the i^{th} mode of elastic waves. The energy of the quantized mode is given by $(n_i + \frac{1}{2})\hbar\,\omega_i$, and energy exchange between such modes and the spins may be described as either emission or absorption of a "phonon" of energy $\hbar\,\omega_i$ by the spin system. The

formalism is quite parallel to that for the radiation field, including the fundamental asymmetry between emission and absorption. The probability of emission (creation) of a phonon of frequency ω_1 by the spin system is proportional to $n_1 + 1$, whereas that of absorption (annihilation) is simply proportional to n_1.

If the lattice temperature is T, the mean value of n_1 is

$$\bar{n}_1 = \frac{1}{e^{\hbar\omega_1/kT} - 1} \tag{5.07}$$

so that emission and absorption probabilities are in the ratio

$$\frac{U_{emission}}{U_{absorption}} = \frac{\bar{n}_1 + 1}{\bar{n}_1} = e^{\hbar\omega_1/kT} \tag{5.08}$$

As with the semiclassical treatment of the radiation field, Section 4, the semiclassical result (5.05) is microscopically reversible and is proportional to the intensity of the effective phonon field. We again identify the semi-classical result with the absorption probability of a full quantum treatment, and the emission probability is to be calculated from Eq.(5.08). Thus, if spin state $\underline{k}$ has greater energy than state $\underline{j}$,

$$\left.\begin{aligned} U_{j\to k} &= \hbar^{-2} \left\langle |(k|f(\vec{r})F_{op}(I,J)|j)|^2 \right\rangle_{av} \; J(\nu_{kj}) \\ U_{k\to j} &= U_{j\to k} \; e^{h\nu_{kj}/kT} \end{aligned}\right\} \tag{5.09}$$

---

* Note that Eq.(5.09) disagrees with BPP's Eq.(30) (which is for the special case of spin 1/2). Although the BPP equation gives the proper ratio of emission and absorption probabilities, each depends upon the zero of the energy scale used in measuring E_p and E_q of BPP Eq.(29). And, of course, if one uses our Eq.(5.08) and the proportionality between H_1^2 and n_1 to express BPP's

transition probabilities in terms of n_1, a peculiar dependence upon n_1 results; e.g., $U_{emission}$ would be proportional to $[n_1(n_1 + 1)]^{1/2}$.

The distinction between solids and liquids, so far as application of Eq.(5.09) is concerned, will usually involve taking $j(\nu)$ to be the normalized Debye spectrum of the familiar classical theory of the specific heat of a solid, on one hand, and to be the correlation spectrum (5.06) on the other. The essential parameter in the first case is the Debye temperature, whereas in the second it is the correlation time.

6. Detailed Balance and Spin Saturation

If spin state k has higher energy than state j, then at thermal equilibrium the principle of detailed balance,

$$N_k U_{kj} = N_j U_{jk} \tag{6.01}$$

combines with Eq.(5.08) to assure a Boltzmann distribution among the spin states.

It is interesting to raise the question whether the principle of detailed balance applies to the spin system in a partially saturated state. Treatises on statistical mechanics often arrive at detailed balance by a classical argument, and none which has come to the authors' attention is clear in a quantum statistical way on whether detailed balance is applicable outside of thermal equilibrium. For our particular problem, the assumption of detailed balance outside thermal equilibrium appears to lead to a contradiction, as is perhaps most easily illustrated for three

levels between any pair of which the selection rules for the interaction effecting relaxation permit transitions.

If N_1, N_2, and N_3 are the level populations, then the steady state solution of Eqs.(3.03) and (3.04) under conditions of detailed balance leads to an expression for N_1-N_2 which can be cast into the form

$$N_1-N_2 = N \frac{W_{23}W_{31} - W_{13}W_{32}}{W_{13}W_{32} + W_{13}W_{23} + W_{31}W_{23}} \qquad (6.02)$$

Now suppose a monochromatic radiation field inducing transitions between 1 and 2 is introduced. Then $W_{12} = U_{12}+V$ and $W_{21} = U_{21}+V$ will be altered, and the other W's remain simply the corresponding U's. We know experimentally that increasing $V_{12} = V_{21} = V$ enables us to diminish N_1-N_2 as much as we please. Yet, by assuming detailed balance, we expressed N_1-N_2 independently of W_{12} and therefore of V.

Another way of expressing this point is to observe that detailed balance requires the condition

$$W_{12}\,W_{23}\,W_{31} = W_{21}\,W_{32}\,W_{13} \qquad (6.03)$$

which becomes, for no rf field,

$$U_{12}\,U_{23}\,U_{31} = U_{21}\,U_{32}\,U_{13}\ . \qquad (6.04)$$

If $V_{12} = V_{21} = V$ is impressed with an external radiation field, then (6.03) becomes

$$(U_{12}+V)\,U_{23}\,U_{31} = (U_{21}+V)\,U_{32}\,U_{13}\ , \qquad (6.05)$$

which cannot hold for all V if $U_{21} \neq U_{12}$.

Of course, the arguments of this section do not include explicit account of direct interaction between the rf field and the

lattice. Although this is usually extremely weak, and is considered not to affect the lattice energy states nor their populations, the U's are in principle altered by this perturbation and a convincing demonstration would have to verify that the U's are not so altered as to keep (6.05) always valid. Our argument is essentially that V can be and is made comparable to or greater than U_{12}, whereas the radiation field-lattice interaction should affect the U's only by a very small (negligible, we think) fraction.

In the analysis of section 3, therefore, the simple conservation of systems, as described by Eqs.(3.03) and (3.04), and the assumption that the presence of V does not alter the U's are used to obtain the saturation factor. There is no question of applying detailed balance, since it is violated by these assumptions.

7. Apparatus and Experimental Procedure.

Fig. 2 is a block diagram of the apparatus used to produce the transitions, detect the resonance, and measure the saturation factor S. The 60Mc/sec rf field is produced in the tank coil of a Colpitts-type oscillator which forms part of a magnetic resonance spectrometer similar in design to that of Schuster.[12] Audio amplifiers

12. N. A. Schuster, Thesis, Washington University (1951).

with a total gain of about a million followed the resonance detector and fed a phase-sensitive detector.[13]

13. N. A. Schuster, Rev Sci. Instr 22, 254 (1951).

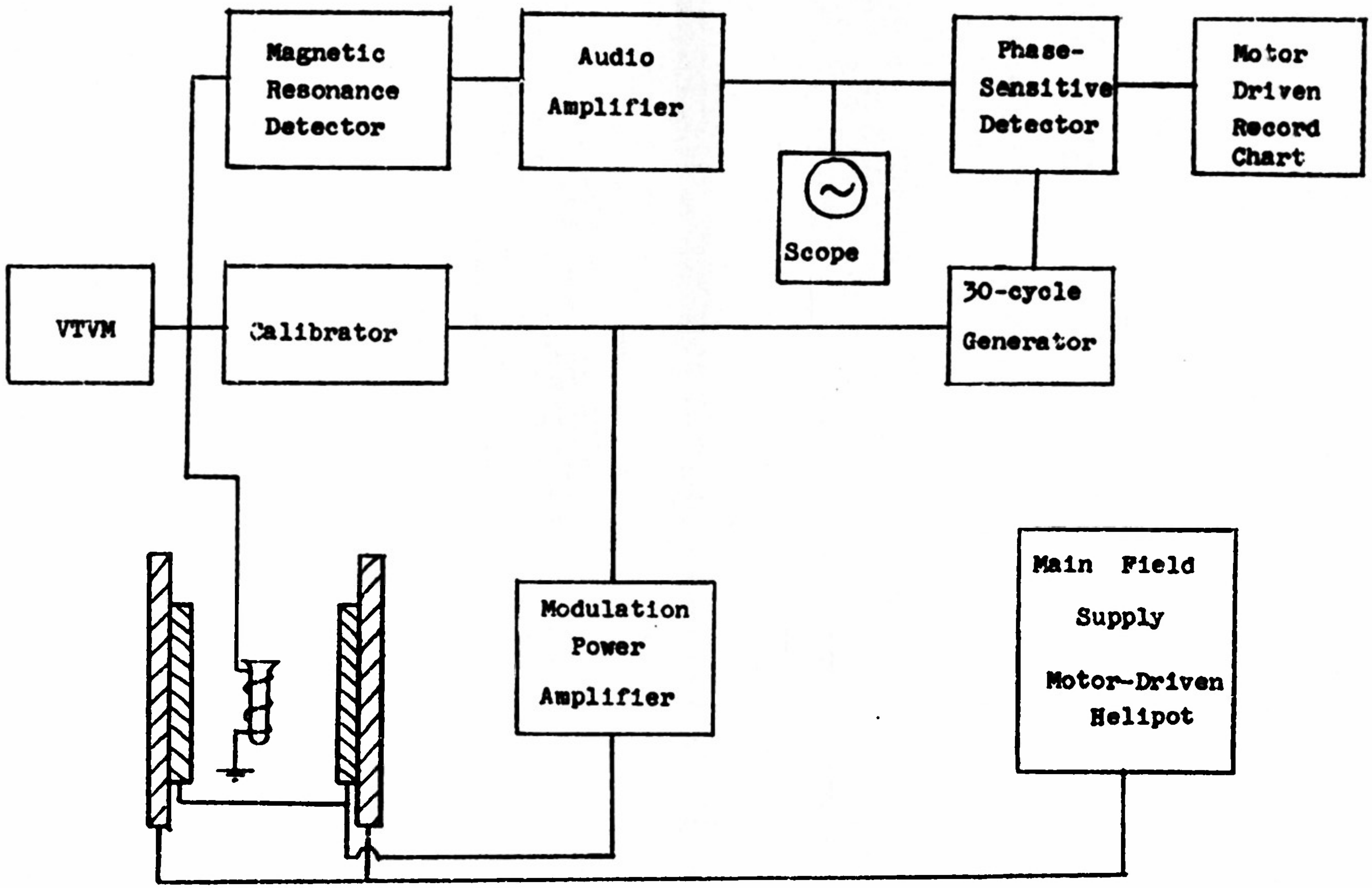


Figure 2. FUNCTIONAL BLOCK DIAGRAM OF APPARATUS

A 30-cycle signal generator produced a square wave reference signal for the phase-sensitive detector and a synchronized sinusoid which, after power amplification, modulated the Helmholtz coil field of about 30 oersteds. This generator also supplied the 30 cycle signal to the grid of the calibrator[14], a device which essentially places the plate resistance of a triode, type 955 in

---

14. G. D. Watkins and R. V. Pound, Phys. Rev. 82, 343 (1951). The authors are indebted to Dr. Watkins for communicating to them further information on his work.

---

this case, across the oscillator tank coil to provide disippation which simulates a non-saturable signal serving as a companion standard for the paramagnetic sample.

In order to know the transition probability (4.07) produced by the oscillator for a given sample, one requires the half-amplitudes H_1 of the rf field at the sample. For this purpose a vacuum tube voltmeter was built into the apparatus to measure the r.m.s. voltage v across the sample coil. The inductance of the coil, which was wound of small flat copper strap to minimize the capacitance between turns, was determined, and the ratio of magnetic field to current in the coil was obtained by performing an auxiliary resonance experiment for which a direct current through the coil produced the external magnetic field for a still smaller coil containing a free radical. The result so obtained is that

$$H_1 = 0.022v \qquad (7.01)$$

A typical measurement of the saturation factor might proceed as follows. The plate voltage of the oscillator is adjusted to provide a low level of oscillation, and the calibrator is set to give a signal equal to that obtained from the paramagnetic sample. The level of oscillation is then increased and a new comparison of calibrator and sample signals is made. In general, the power level and changes in the properties of the oscillator circuit at the new oscillation level will alter the absolute signal intensity, but these changes will affect equally the signal from a given dissipative load across the coil, whether of paramagnetic or calibrator origin, and the relative intensity is meaningful. If the calibrator and the sample still produce the same relative signal, then S is still unity and saturation has not set in. The oscillation level is then further increased until a curve of $\underline{S}$ $\underline{\text{versus}}$ $\underline{v}$, the r.m.s. coil voltage, is plotted; by means of Eq.(7.01) such a curve can be converted to $\underline{S}$ $\underline{\text{versus}}$ $\underline{H}_1$.

The shape function $g(\nu)$ required to calculate V_{jk} from (4.07) is determined from the measured resonance curves at low power (where $S \cong 1$). Since the modulation technique is used, the line profile actually measured is proportional to the derivative $dg/d\nu$. Of course, the calibrator triode is supplied with a 30 cycle grid signal to provide a standard signal coherent with the phase-sensitive detector reference voltage.

8. Experimental Results

Aqueous solutions of $K_2\,ON(SO_3)_2$ are unstable and often become diamagnetic in a matter of several minutes, the decay products catalyzing the spin-pairing reaction. It was found that making the solution about 0.1 normal in Na_2CO_3 stabilizes the free radical solution in a pH range proper to prevent appreciable deterioration for several days.* In this way, measurements were easily made on samples containing various concentrations of $ON(SO_3)_2^{--}$ ion.

*We are indebted to Professor Weissman of the Washington University department of chemistry for this discovery.

All measurements reported here were made at 60 Mc/sec for the transition $(F = 3/2,\ m_F = -3/2) \longleftrightarrow (F = 3/2,\ m_F = -1/2)$, which is transition $4 \leftrightarrow 3$ on Figure 1. This transition was selected because its frequency <u>versus</u> field characteristic does not depart sufficiently from linearity to complicate width measurements, as may happen for those transitions having small $d\nu/dH$, and because it is reasonably intense. This transition gives, at a fixed microwave frequency, the hyperfine triplet which occurs in the highest external field.

Fig. 3 graphs experimental points for the derivative of the resonance absorption of a 0.02 M aqueous solution of $ON(SO_3)_2^{--}$ at 60 Mc/sec. Also placed on the graph field is a curve corresponding to the derivative of a so-called Lorentz[15] or damped-oscillator

15. Pake and Purcell, Phys. Rev. 74, 1184 (1948).

LORENTZ LINE : $$\chi'' = \chi''_{max} \frac{1}{1 + \left(\frac{H - H_0}{\delta H}\right)^2}$$

DERIVATIVE : $$\frac{d\chi''}{dH} = -\frac{2\chi''_{max}}{\delta H} \frac{(H - H_0)/\delta H}{\left[1 + \left(\frac{H - H_0}{\delta H}\right)^2\right]}$$ (Solid line)

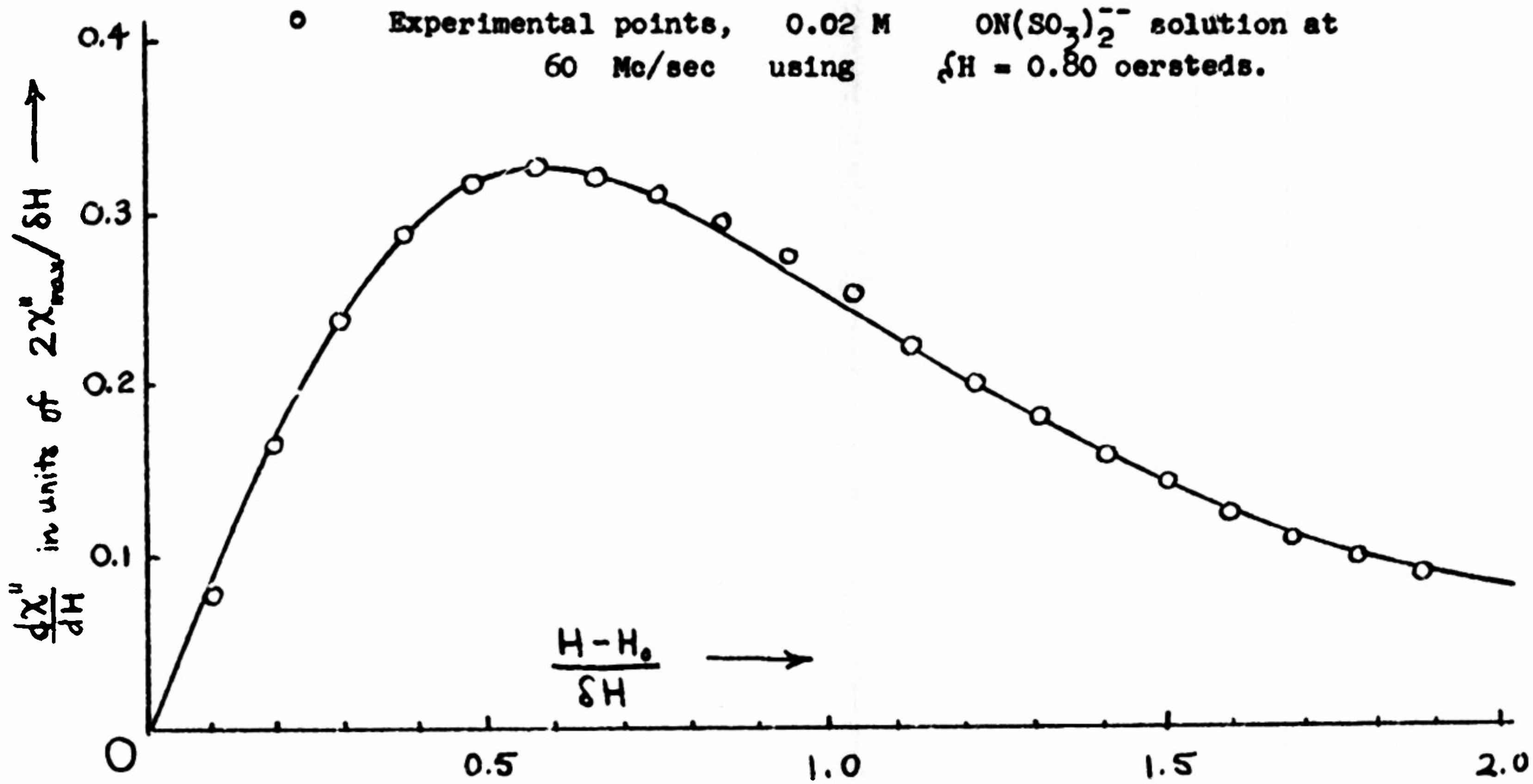


FIG. 3

line shape function. It is seen that the Lorentz curve approximates very well to the experimental points.

In our analysis of the experimental saturation data, we follow BPP, whose equations* can be adapted to show that for our

---

* Reference 7, section IV, Eq.(17). The BPP saturation parameter <u>s</u> is our V/W_R.

---

situation (BPP case I: the modulation frequency is much less than W_R) the decline in the derivative extremum under saturation is given by a saturation factor

$$S' = \frac{d\chi''(H_1)}{d\nu} \Big/ \frac{d\chi''(H_1 \to 0)}{d\nu} = \left[1 + V/W_R\right]^{-3/2} = S^{3/2} \tag{8.01}$$

Note that S' is not a derivative of S. The value of V to be used in this expression is its maximum at the resonance center, thus corresponding to the maximum value of $g(\nu)$. For a Lorentz line, $g(\nu)_{max}$ is $1/\pi$ times the reciprocal of the half-width $\delta\nu$ at half-maximum intensity on the unsaturated $g(\nu)$ curve. If one measures experimentally the width, in magnetic field units, between points of extreme slope, the conversion between the measured quantity ΔH and $g(\nu)_{max}$ is, for the Lorentz shape function shown on Fig. 3,

$$g(\nu)_{max} = \frac{4}{\sqrt{3}}(\gamma\Delta H)^{-1} \tag{8.02}$$

where $\gamma = d\omega/dH$ is obtained from the (angular) frequency <u>versus</u> field characteristic for the transition in question. The parameter δH of Fig. 3 is, in terms of the width between inflction points, $(\sqrt{3}/2)\Delta H$.

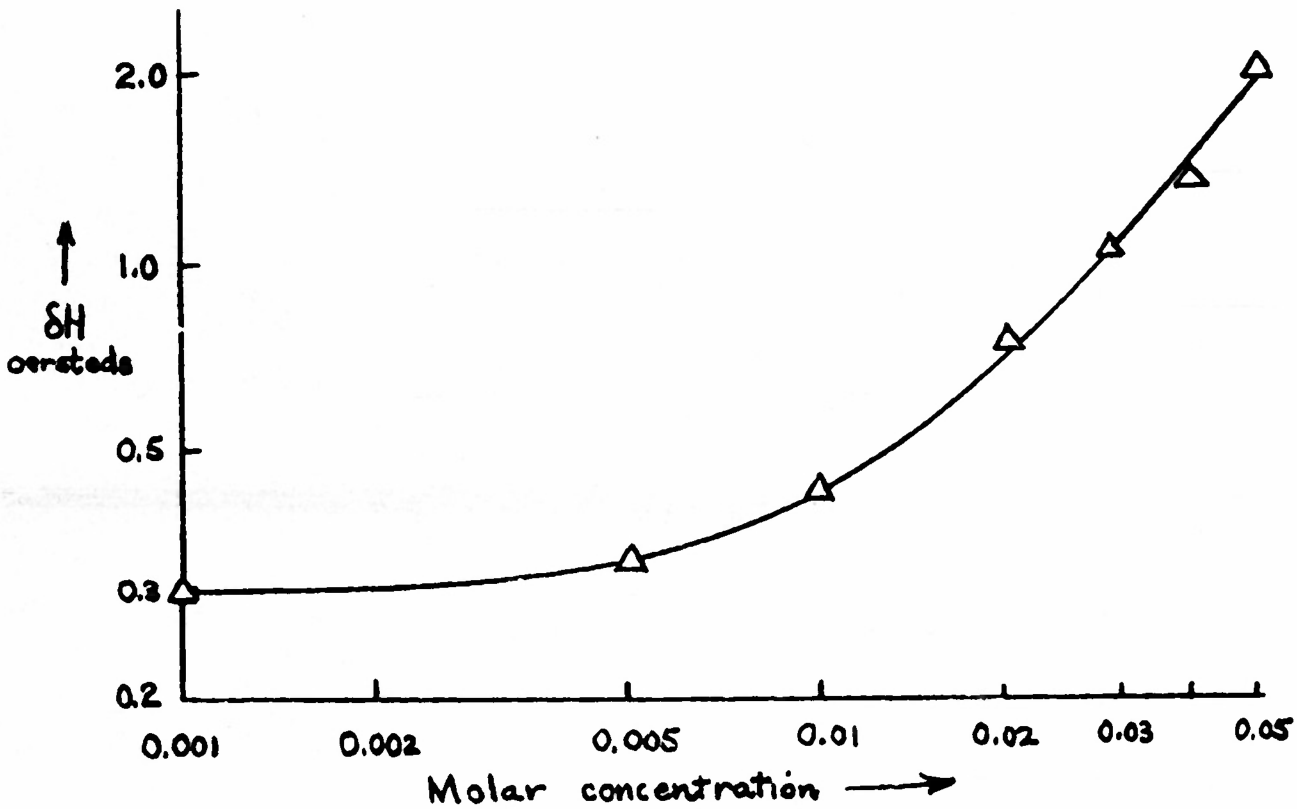


Fig. 4

Line width *versus* molar concentration of $ON(SO_3)_2^{\cdot -}$ ion in aqueous solution. Transition excited is that between levels 4 and 3 of Fig. 1.

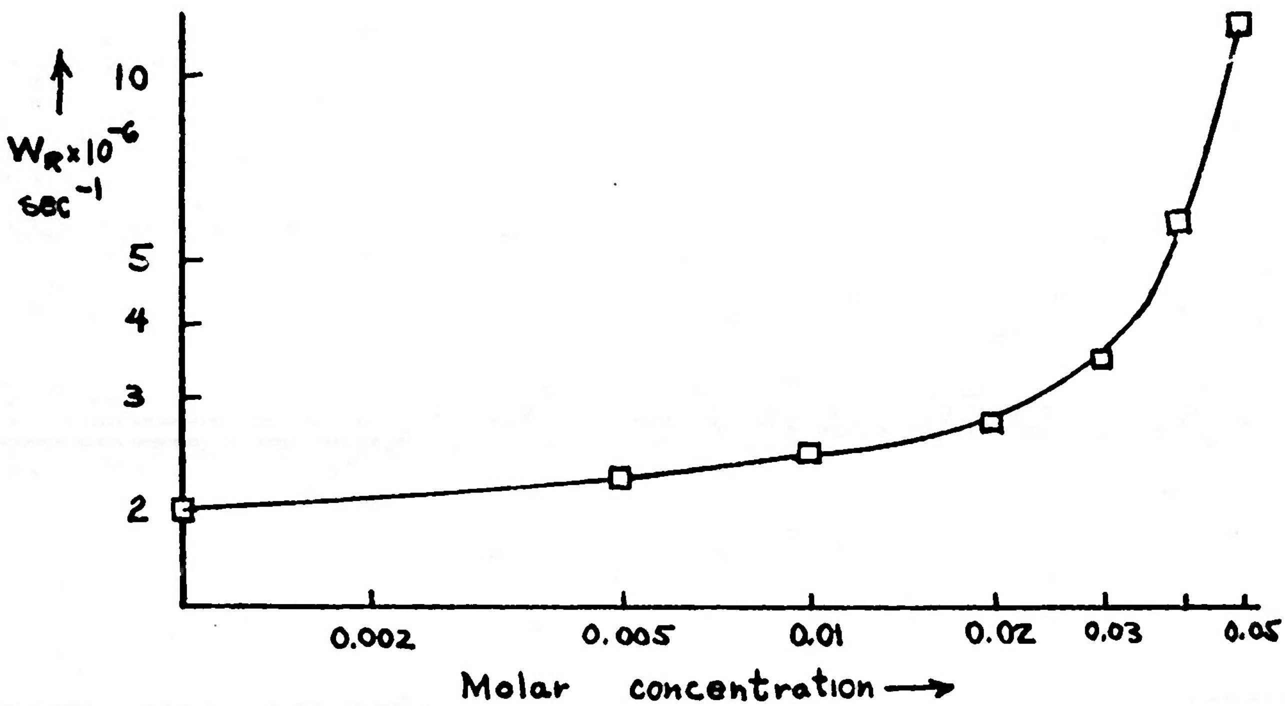


Fig. 5

Relaxation probability *versus* molar concentration of $ON(SO_3)_2^{--}$ ion in aqueous solution. Transition saturated in making these measurements is that between levels 4 and 3 of Fig. 1.

Figures 4 and 5 plot respectively the experimental values of δH and of the relaxation probability W_R <u>versus</u> the molar concentration of $ON(SO_3)_2^{--}$ ion. At concentrations above 0.5 M, the hyperfine structure begins to give way to a single broad line. The lower limit of the concentration range is determined by the decline in signal sensitivity as fewer and fewer free radicals are present in the sample.

A striking feature of Figures 4 and 5 is that both the line width and relaxation probability appear to approach asymptotically a concentration independent value. The relaxation probability, through its limitation of the life-time of a spin state, should contribute an amount the order of W_R/γ to the total line width. The low-concentration value of W_R/γ gives about 0.7 oersteds. This is quite comparable to the asymptotic low-concentration line width of 0.3 oersteds, and it indicates that the relaxation processes may well determine the entire line width. If such is the case, we will understand both Figures 4 and 5 if we can explain the concentration independent relaxation probability.*

---

* Depending upon the relationship which one assumes should exist between W_R and its contribution to δH, the fact that W_R/γ <u>exceeds</u> δH may cause some concern for the internal consistency of our measurements; the line cannot be sharper than the uncertainty principle would allow. However our procedure of calibrating the rf coil (section 7) when it carries direct current is not beyond reproach, inasmuch as the current distribution throughout the cross-section of the copper strap at 60 Mc/sec is certainly somewhat different from the d.c. distribution. Therefore a factor of perhaps 2 must be allowed in our absolute values of W_R; relative values should be good within 10 percent or better.

In order to test the possibility that the nuclear moments of the water solvent might provide the interaction which relaxes the free radical spins, the low-concentration measurements of Figures 4 and 5 were made for solutions of $ON(SO_3)_2^{--}$ in D_2O. Although the deuteron magnetic moment is about 0.3 that of the proton, the curves for the D_2O solution were indistinguishable from those of Figures 4 and 5. We thus have experimental indication that the nuclear moments of the solvent do not provide the relaxation mechanism.

9. The Saturation Factor for the Transition Studied.

In order to compare postulated relaxation mechanisms with the measured value of W_R, we require the expression for W_R in terms of the U's for $ON(SO_3)_2^{--}$. There are six homogeneous equations of the form (3.03) for a system with the energy levels of Figure 1. For magnetic dipole transitions in the radiofrequency range, the Boltzmann factors associated with emission (Eq. (5.08)) usually depart from unity by less than 10^{-4}. Furthermore, BPP find for water at room temperature that $\tau_c = 4 \times 10^{-12}$ sec. In 31.4 oersteds, all transitions permitted between the levels of Figure 1 occur at frequencies of 10^7 or 10^8 $\sec^{-1}$. By Eq.(5.06), the resulting correlation spectrum $J(\nu)$ is essentially "white" with intensity $2\tau_c$ per unit frequency range.

Comparison of relative values of the coefficients in the six homogeneous equations may therefore by made from

$$U_{jk} = \hbar^{-2} \left\langle f(r)^2 \right\rangle_{av} \left| (k|\vec{\mu}|j) \right|^2 2\tau_c \qquad (9.01)$$

in which the operator function F_{op} of Eq.(5.05) is

$$\vec{\mu} = -g_J \mu_o \vec{J} + g_I \mu_o \vec{I} \approx -g_J \mu_o \vec{J} \qquad (9.02)$$

and its matrix elements are to be calculated using the spin functions (1.02) which apply for 31.4 oersteds. Such non-vanishing values of $|(k|J_x|j)|^2$ for the π transitions and $|(k|J_z|j)|^2$ for σ transitions are tabulated below in decreasing order:

j	k	$\|(k\|J_x\|j)\|^2$	$(k\|J_z\|j)^2$
3	5		0.350
1	6	0.237	
3	4	0.226	
2	5	0.224	
2	6		0.190
4	5	0.024	
2	3	0.023	
1	2	0.012	
5	6	0.011	
3	6	0.001	

Magnetic dipole transitions between level pairs 1 and 3, 1 and 4, 1 and 5, 2 and 4, and 4 and 6 are forbidden. In addition we shall neglect the three weakest permitted transitions (3 to 6, 5 to 6, and 1 to 2) in solving for S_{43}. After so doing, one finds for S_{43} an equation of the type of (3.09) with $W_R(43)$ given by

$$W_R(43) = U_{43} + U_{45}\,\frac{U_{23}U_{35} + U_{23}U_{25} + U_{25}U_{35}}{U_{23}U_{35} + U_{23}U_{45} + U_{23}U_{25} + U_{25}U_{45} + U_{25}U_{35}} \qquad (9.03)$$

Here we have dropped "thermal differences", i.e., $U_{jk} - U_{kj}$, in comparison with $U_{i\ell}$; this may be done as soon as the equations are placed in a form corresponding to (3.06) and it greatly simplifies solution.*

---

* It is useful to note that the form of the equations and the fact that W_R must depend upon quantities of zero order in "thermal differences" allows one to set up an analogy with a passive network of conductances. Branch points in the analog network correspond to the energy states of the system, and the conductance between j and k corresponds to U_{jk}. This is perhaps the simplest method for calculating W_R in a particular case.

The error in dropping the three weak transitions is evidently not serious, since the correction to U_{43} in Eq.(9.03) is, for an isotropic white radiation bath, easily shown from the table to be about 10 percent of U_{43}. Errors of 10 percent or so can easily creep into saturation measurements of W_R.

10. The Relaxation Mechanism at the Higher Concentrations.

At the high concentration end of the curves of Figures 4 and 5, one expects ion-ion collisions to effect relaxation and W_R should be proportional to concentration. Although the log-log plot of Figure 4 appears to approach a slope measurably greater than unity, one should not attach too much importance to it, for this is the region in which the hyperfine splitting is about to blur into a single broad line. The tails of the three high frequency transitions overlap appreciably and the width of an individual line is difficult to measure.

As a check on the mechanism, one should obtain an approximately correct order of magnitude for W_R from the BPP Eq.(50), intended to be used to calculate the contribution to W_R for hydrogen nuclei through their interaction with neighboring water molecules:

$$W_R \simeq \frac{9}{2} \pi^2 g^4 \beta^4 \hbar^{-2} \eta N_0/5kT \qquad (10.01)$$

Here η is the viscosity, which we take for our solution to be that of water at room temperature, about 10^{-2} c.g.s. units. For 0.05 molar, N is 3×10^{19} cm^{-1} and Eq. (10.01) gives $W_R = 1.5 \times 10^7$ sec^{-1}.

The actual measured value is $W_R = 4 \times 10^7$ sec^{-1}. This is probably adequate agreement considering that we have made the approximation of free electrons by neglecting the nuclear moment coupling and that we have approximated the viscosity of the $ON(SO_3)_2^{--}$ ion. These approximations, however, seem if anything to be in the direction of worsening the agreement, and there is a likelihood that the lines appear to be abnormally wide at concentrations just below that at which the component hyperfine lines merge.

11. Interaction with the Nuclear Moments of the Solvent.

Although both D_2O and H_2O had the same effect as solvents, we shall estimate the contribution to W_R to be expected for this mechanism and check the theory by noting whether the result is negligible in comparison with our measured W_R.

The dipole interaction between the $\underline{i}^{th}$ hydrogen nucleus of the solvent and the $\underline{j}^{th}$ ionic spin is

$$\mathcal{H}_{ij} = \vec{\mu}_i \cdot \vec{\mu}_j \, r_{ij}^{-3} - 3(\vec{\mu}_i \cdot \vec{r}_{ij})(\vec{\mu}_j \cdot \vec{r}_{ij}) \, r_{ij}^{-5} \qquad (11.01)$$

where

$$\vec{\mu}_i = g_I \, \mu_o \, \vec{I}_i$$
$$\vec{\mu}_j = -g_J \, \mu_o \, \vec{J}_j \qquad (11.02)$$

Following BPP, we may write

$$\mathcal{H}_{ij} = -g_I \, g_J \, \mu_o^{\,2} \left[A+B+C+D+E+F\right], \qquad (11\ 03)$$

where

$$A = J_{zj} \, I_{zi} \, (1-3 \cos^2 \theta_{ij}) \, r_{ij}^{-3}$$
$$B = -\tfrac{1}{4} \left[J_{+j} \, I_{-i} + J_{-j} \, I_{+i}\right] (1-3 \cos^2 \theta_{ij}) \, r_{ij}^{-3}$$
$$C = -\tfrac{3}{2} \left[J_{zj} \, I_{+i} + J_{+j} \, I_{zi}\right] \sin \theta_{ij} \cos \theta_{ij} \, e^{-i\varphi_{ij}} \, r_{ij}^{-3}$$
$$D = -\tfrac{3}{2} \left[J_{zj} \, I_{-i} + J_{-j} \, I_{zi}\right] \sin \theta_{ij} \cos \theta_{ij} \, e^{i\varphi_{ij}} \, r_{ij}^{-3}$$
$$E = -\tfrac{3}{4} \, J_{+j} \, I_{+i} \sin^2 \theta_{ij} \, e^{-2\varphi_{ij}} \, r_{ij}^{-3} \qquad (11.04)$$
$$F = -\tfrac{3}{4} \, J_{-j} \, I_{-i} \sin^2 \theta_{ij} \, e^{+2\varphi_{ij}} \, r_{ij}^{-3}$$

Symbols I_{+i} and J_{-j} denote the respective raising and lowering operators: $I_{+i} = I_{xi} + iI_{yi}$ and $J_{-j} = J_{xj} - iJ_{yj}$.

As an example, consider the contribution of term E from a proton at distance r:

$$U_{43}^{(E)}(r) = g_I^2 \, g_J^2 \, \mu_o^4 \, \hbar^{-2} \sum_{m_i, m_i'} G_{m_i} \left\langle \left| (3;m_i'|E|4;m_i) \right|^2 \right\rangle_{av} \, j\left(\frac{W'-W}{\hbar}\right) \qquad (11.05)$$

where $W' = W_3 - g_I \, \mu_o \, H \, m_i'$ and $W = W_4 - g_I \, \mu_o \, H \, m_i$.

We denote by G_{m_i} the fraction of protons in state m_i, and by W_3 and W_4 the energies corresponding to the levels so numbered in Figure 1. The nuclear contributions to W' and W are necessary to conserve energy for the transitions, but may be neglected in practice. Therefore $j\left(\frac{W'-W}{\hbar}\right) = 2\,\tau_c$ as indicated in Sec. 9.

Apart from terms of order $g_I\,\mu_o\,H/kT$ (about 10^{-9} in 30 oersteds), $G_{m_i} = \frac{1}{2}$ for both spin states of the protons within a thin shell at distance r. In order to consider all protons of the solvent, whatever the value of r, we follow BPP by assuming that $\tau_c = r^2/12D$, D being the diffusion constant, and integrating from the distance of closest approach, r_o, throughout the solvent. If there are N_o solvent protons per unit volume, the contribution of E is

$$U_{43}{}^{(E)} = g_I^2\, g_J^2\, \mu_o^4\, \hbar^{-2}\, \frac{1}{2} \sum_{m_i, m_i'} \left|(3;m_i'\right| - \tfrac{3}{4}\, J_{+j}\, I_{+i}\left| 4;m_i)\right|^2 \qquad (11.06)$$
$$\times \left\langle \left|\sin^2\theta_{ij}\, e^{-2i\phi_{ij}}\right|^2 \right\rangle_{av}\; N_o \int_{r_o}^{\infty} r^{-6}(2r^2/12D)\, 4\pi r^2 dr$$

Performing the indicated sums and integrations and taking the averages of the angle functions, one obtains

$$U_{43}{}^{(E)} = \frac{\pi}{5}\, g_I^2\, g_J^2\, \mu_o{}^4\, \hbar^{-2}\, c^2\, N_o/Dr_o \qquad (11.07)$$

The diffusion constant is presumably not quite the same as for self-diffusion of pure water. However, we postulate a kind of equivalent viscosity, η, related to r_oD through Stokes law:

$$\frac{1}{Dr_o} = \frac{6\pi\eta}{kT} \qquad (11.08)$$

Then

$$U_{43}^{(E)} = \pi^2 g_I^2 g_J^2 \mu_0^4 \hbar^{-2} N_0 \eta c^2/kT \qquad (11.09)$$

For pure water, $\eta = 10^{-2}$ c.g.s. units near room temperature; lacking any other value, we use this for our solution. From section 1, we find $c^2 = 0.903$. Finally the relaxation probability obtained from (11.09) is

$$W_R^{(E)} \cong 3 \times 10^4 \text{ sec}^{-1} \qquad (11.10)$$

for a dilute aqueous solution of $ON(SO_3)_2^{--}$ ion. This result is indeed consistent with the conclusion from comparison of H_2O and D_2O as solvents: the interaction with solvent nuclear dipole moments is negligible in relation to the measured W_R of 2×10^6 sec^{-1}.

12. Relaxation through the N^{14} Quadrupole Moment

The odd electron, which of course possesses no quadrupole moment, is magnetically coupled to the N^{14} nucleus, which has a quadrupole moment. The relaxation probability contributed by the N^{14} nucleus can also be shown to be negligible.

We deliberately overestimate this contribution to W_R by supposing for argument's sake that the entire electric quadrupole interaction of the N^{14} nucleus with fluctuating electric field gradients is effective in relaxing the electron spin. Actually such relaxation can occur only in low magnetic fields where the coefficients b and d entering into the linear combinations (1.02) of spin functions are appreciable. An order of magnitude upper limit to W_R from this interaction is therefore, following Eqs. (5.05), (5.06)

$$W_R \sim \hbar^{-2} (eQ)^2 \left\langle \left(\frac{\partial^2 \phi}{\partial z^2}\right)^2 \right\rangle_{av} 2\tau_c \qquad (12.01)$$

in which Q is the N^{14} quadrupole moment and Φ is the electric scalar potential at the nucleus.

Accurate evaluation of a representative component of the electric field gradient has not been made, even for a rigid lattice, and equally little is known about the average square of such a component for a liquid. However, Bloembergen[16] found that the

16. N. Bloembergen, Thesis, University of Lieden (1948).

deuteron effected nuclear relaxation in liquid D_2O, and that the electric field gradient has a magnitude essentially that at 1Å or 2Å from an electronic charge. For an estimate, we take er^{-3}, with $r = 1$Å, as the magnitude of $\frac{\partial^2 \Phi}{\partial z^2}$. The value of Q for N^{14} is about 10^{-26} cm^2. Taking $\tau_c \cong 10^{-11}$ sec., one finds that $W_R \sim 10^{+3}$ sec^{-1}, which is again much smaller than the observed value, 2×10^6 sec^{-1}.

13. The Role of Spin-Orbit Coupling

In 1936, Kronig[17] proposed that unaccountably short

17. R. deL. Kronig, Physica 6, 33 (1936).

relaxation times in certain alums could be explained by considering the important role played by spin-orbit coupling. The modulation of the spin-spin interaction by the lattice vibrations, considered in Waller's pioneering theory[18] of spin-lattice relaxation proved

18. I. Waller, Zeits. f. Physik 79, 370 (1932)

entirely inadequate to explain observed relaxation times. Another possibility, the modulation of the crystalline Stark splitting by the lattice vibrations, appears at first sight to hold no promise for relaxation in those substances which possess only Kramers degeneracy in the ground state. However, through the spin-orbit coupling, the modulation of the Stark splitting is felt by the spins.

Van Vleck[10] extended and refined Kronig's ideas in his monumental calculation of relaxation times for titanium and chrome alums. Two processes are distinguished. One, the so-called direct process, gives a highly field dependent relaxation time which ought to apply at a few degrees Kelvin, but was found to be still too large. The second, or Raman, process is effective in zero as well as in non-vanishing external magnetic fields. It depends upon the inelastic scattering of high energy vibrational quanta by the spin systems, with the spin system absorbing or emitting a vibrational quantum of very low energy relative to the original vibration quantum. Although this is a second order process compared to the direct process, it is important because the entire elastic spectrum, rather than a narrow portion at its weak end, is called into play. In fact, the Raman process probably dominates at all but the lowest temperatures.

It is a simple matter[17] to illustrate the influence of a spin-orbit term $\lambda\vec{L}\cdot\vec{S}$ on Stark orbitals which possess only spin degeneracy. The spin-orbit interaction renders incomplete the quenching of orbital angular momentum by the crystalline electric field, and, as a result, the spectroscopic splitting factor[19] departs from the free electron value, $g_e = 2.0023$, by an amount

---

19. C. Kittel, Phys. Rev. 76, 743 (1949)

the order of λ/Δ , where Δ is the Stark interaction.

It is less simple to demonstrate the existence, via the Raman Process, of relaxation caused by modulation of the Stark splitting in the presence of the spin-orbit term $\lambda\vec{L}\cdot\vec{S}$. In fact, Kronig's model, as pointed out by Van Vleck[10], yields vanishing transition probabilities even when pursued to second order in the orbit-lattice modulating interaction. The vanishing in first order is to be expected, but that in second order appears to be due to a concellation of terms which would not cancel if the inherent quantum asymmetry between emission and absorption probabilities (see sections 4 and 5) were contained in the calculation. Van Vleck includes this by use of quantized normal modes for the cluster of H_2O molecules about the Ti^{++} ion, and he finds a non-vanishing result in second order (third order, in reference 10, inasmuch as the zero order functions used do not yet include the effect of the $\lambda\vec{L}\cdot\vec{S}$ coupling).

In the present problem, we have no knowledge of the normal modes of the liquid "lattice". In fact, the free radical ion presents several complications. The ion itself is not spherically symmetric. When such is the case, as pointed out by Mizushima and Koide[20] and

20. Mizushima and Koide, Jour. Chem. Phys. 20, 765 (1952).

suggested independently by H. Primakoff, the spin-orbit interaction is not simply proportional to $\vec{L}\cdot\vec{S}$. The Dirac equation, after elimination of the small component wave functions, yields two interaction terms[21] which may be included[22] in the spin-orbit interaction:

21. L. I. Schiff, Quantum Mechanics (McGraw-Hill, 1949).

22. Reference 9, page 130

$$\mathcal{H}_{\text{spin-orbit}} = -\frac{\hbar^2}{4m^2c^2}(\text{grad } V)\cdot\text{grad} + \frac{\hbar}{4m^2c^2}\vec{s}\cdot(\text{grad } V)\times\vec{p}\ ; \qquad (13.01)$$

the potential energy function for the electron is $\underline{V}$, $\vec{s}$ is the electron spin and $\vec{p}$ is its linear momentum operator. A proper accounting of spin-orbit effects would thus require use of (13.01) instead of $\lambda\vec{L}\cdot\vec{S}$.

A second complication is that, for the $ON(SO_3)_2^{--}$ ion in aqueous solution, we may justifiably think of two sources for the orbit-lattice interaction which modulates the Stark splitting for the odd electron. One source involves the internal vibrations of the ion itself which produces fluctuating local electric fields over the orbit of the electron, and the other is the solvent as its randomly moving water dipoles also produce fluctuating local fields over the electron orbit.

Whereas a theoretical investigation of the interaction (13.01) presents grave difficulties for a free radical ion about which we know so little concerning the odd electron wave function, experiment may be able to distinguish which source of the orbit-lattice interaction is dominant, provided, of course, that spin-orbit coupling is involved in determining the W_R value measured experimentally. In order to shed some light on this important question, we brush aside our ignorance of the quantum nature of the motions and suppose that, for some fortuitous reason, the spectrum of their vibrations influences the Raman processes for

$ON(SO_3)_2^{--}$ approximately as it does for Ti^{++} in Titanium alum. For the latter Van Vleck obtains about 10^9 sec^{-1} as the reciprocal relaxation time (which is essentially our W_R) due to Raman processes at normal temperatures and low fields. The matrix element in the transition probability is proportional to λ/Δ^3, where Van Vleck takes Δ, the Stark splitting, to be about 1000 cm^{-1} and λ/Δ to be about 1.5×10^{-1}. For free radicals, Δ may well be about the same as for titanium alum, but λ/Δ is much smaller; the spectroscopic splitting factor for $ON(SO_3)_2^{--}$ is 2.0055, measured in high fields[23], indicating that $\lambda/\Delta \approx 10^{-3}$.

---

23. J. Townsend, unpublished

Since W_R is proportional to the square of the matrix element, our utterly curde adjustment of the titanium result simply scales it down by the square of the ratio of the respective λ's, giving $W_R \sim 10^5$ sec^{-1}. In view of the high power of Δ involved and our wild approximations, this can hardly be called disagreement with the measured W_R, 2×10^6 sec^{-1}.

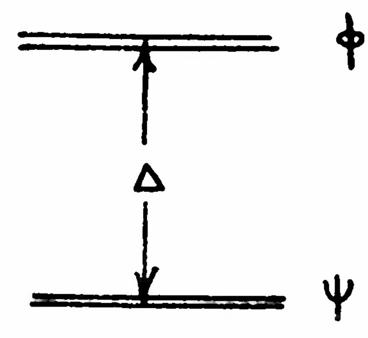
It is thus entirely possible that spin-orbit effects do lead to the observed W_R, and experiments are underway in this laboratory to examine whether it may be the solvent or the internal vibration of the ion which provides the orbit-lattice interaction.

14. Relaxation Through Statistical Processes of Second Order.

An interesting possibility for relaxation is brought out by our detailed expression (3.09) for the relaxation probability.

In Van Vleck's calculation, discussed in the previous section, the quantity estimated corresponds only to U_{21}, and nothing has yet been said about the remaining function of U's in Eq.(3.09). Although this function may, as in section 9, normally be small compared to U_{21}, such may not be the case if one must go to second or higher orders to obtain a non-vanishing U_{21}. Physically, this means that a relaxation mechanism which does not produce direct transitions between the levels under consideration may still effect relaxation by first carrying systems to a third level and then to the second. Such a process is second order in a statistical rather than a perturbation theory sense, i.e., energy is conserved for both transitions, whereas the second order quantum perturbation transition probability does not require energy conservation for the intermediate state.

The simple model of Kronig[17] is adequate for application of this idea to a free radical ion with spin-orbit coupling. We suppose that the odd electron of $ON(SO_3)_2^{--}$ is subject to a molecular Stark field which splits the orbital states into widely separated levels. For simplicity, we follow Kronig by supposing that the two lowest of these are separated by energy Δ whereas the others have very much higher energies. Each of these levels retains its spin degeneracy. Let these orbital states be ψ and ϕ. Then, if α and β refer to spin states $+\frac{1}{2}$ and $-\frac{1}{2}$ respectively, the effect of a spin-orbit interaction $\lambda\vec{L}\cdot\vec{S}$ is, to first order in $\frac{\lambda}{\Delta}$, to produce the following mixtures of the unperturbed functions $\psi\alpha$, $\psi\beta$, $\phi\alpha$, and $\phi\beta$:



$$\begin{aligned}
\Psi_1 &= \psi\alpha - \frac{\lambda}{\Delta} b\,\phi\alpha - \frac{\lambda}{\Delta} a\,\phi\,\beta \\
\Psi_2 &= \psi\beta + \frac{\lambda}{\Delta} a^*\phi\alpha + \frac{\lambda}{\Delta} b\,\phi\,\beta \\
\Psi_3 &= \phi\alpha - \frac{\lambda}{\Delta} b\,\psi\alpha - \frac{\lambda}{\Delta} a\,\psi\,\beta \\
\Psi_4 &= \phi\beta + \frac{\lambda}{\Delta} a^*\psi\alpha + \frac{\lambda}{\Delta} b\,\psi\,\beta
\end{aligned} \tag{14.01}$$

Here,

$$\begin{aligned}
a &= \frac{1}{2}\int \phi\,(L_x + iL_y)\,\psi\,d\tau \\
b &= \frac{1}{2}\int \phi\; L_z\,\psi\,d\tau \qquad = -b^*
\end{aligned} \tag{14.02}$$

In (14.02), ϕ is not denoted complex conjugate since, under the conditions of quenched orbital angular momentum, $\int \phi\vec{L}\phi\,d\tau = \int \psi\vec{L}\psi\,d\tau = 0$, it is possible to express ϕ and ψ as real numbers.[17]

If one sets up Eqs.(3.03) and (3.04) and solves for the saturation factor and for W_R associated with transitions between Ψ_1 and Ψ_2, he finds the following result:

$$W_R^{(12)} \simeq \frac{1}{2} U_{14} \tag{14.03}$$

In obtaining (14.03), one uses $U_{12} = 0 = U_{34}$, as obtained from Eqs.(14.01). Also, in terms of absorption probabilities, these wave functions yeild

$$U_{13}/U_{14} \sim U_{23}/U_{24} \sim (\lambda/\Delta)^2 .$$

The relation (5.09) between absorption and emission holds, e.g.,

$$U_{41} = U_{14}\, e^{\Delta/kT} . \tag{14.04}$$

Here, contrary to cases previously cited, the exponential factor is far from unity if Δ corresponds to about 1000 cm^{-1} ($\Delta/kT \sim 5$ at

room temperature) and the result for W_R has been simplified by dropping absorption probabilities relative to emission probabilties.

We can evaluate U_{14} from Eq.(5.09) in which it must be recalled that we now require $j(\nu_{jk})$ at $\nu_{jk} = \Delta/h \approx 3 \times 10^{13}$ sec^{-1}. If we take $F_{op}(I,J) = 1$ in Eq.(5.09) and denote

$$\left\langle \left|(4|f(\vec{r})|1)\right|^2 \right\rangle_{av} = \left|\frac{\lambda}{\Delta} a\right|^2 \left\langle \left| \int \psi f(\vec{r}) \psi d\tau - \int \phi f(\vec{r}) \phi d\tau \right|^2 \right\rangle_{av}$$

$$= \left|\frac{\lambda}{\Delta} a\right|^2 \delta^2 , \qquad (14.05)$$

where δ^2 is a measure of the mean square of the electric interaction $f(r)$ which modulates the Stark effect, then, by Eq.(5.09)

$$U_{14} = \hbar^{-2} |a|^2 \left(\frac{\lambda}{\Delta}\delta\right)^2 j\left(\frac{\Delta}{h}\right) \qquad (14.06)$$

Since $|a|^2 \approx 1$ and $j(\Delta h) \approx \dfrac{1}{2\pi \Delta^2 \tau_c / h^2}$ for $\Delta/h > 1/\tau_c$,

we have

$$W_R = \frac{1}{2} U_{14} \approx \left(\frac{\lambda}{\Delta}\right)^2 \left(\frac{\delta}{\Delta}\right)^2 \frac{1}{\tau_c} \qquad (14.07)$$

Taking $W_R = 2 \times 10^6$ sec^{-1}, $\lambda/\Delta = 10^{-3}$, and $\tau_c = 10^{-11}$ for water solutions at room temperature, one finds that, if this mechanism is to be adequate, δ/Δ would have to be the order of unity. It is not unreasonable that the fluctuating Stark interaction arising from motions of the strong water dipoles or the internal vibrations of the ion might be comparable to the static Stark interaction, although the perturbation procedure would be somewhat strained in that event.

Again, the crudeness of our estimate does not lead us to very positive conclusions, but relaxation via the statistical second

order processes is not ruled out.

Whether quantum mechanical or statistical second order processes are involved in determining W_R, the experiments now in progress, which are aimed at distinguishing between the source of the modulating Stark field (intense vibrations in the ion or Brownian motions of the solvent), will serve a useful purpose.

15. Summary

In water solutions of the free radical ion $ON(SO_3)_2^{--}$, width of the paramagnetic resonance seems to be determined by relaxation processes, at least for solutions sufficiently dilute to exhibit well resolved hyperfine structure. The achievement of statistical equilibrium among the various hyperfine levels in low magnetic fields is more complex than in a simple two-level system. Where saturation methods are used, the relaxation probability is suggested as a more precisely defined quantity than the relaxation time.

At very low concentrations, the relaxation probability for the particular transition studied reaches a concentration independent value of 2×10^6 sec^{-1}. Interaction between the free radical and nuclear dipoles of the solvent is proved an inadequate mechanism both experimentally and theoretically. The interaction of the N^{14} quadrupole moment of $ON(SO_3)_2^{--}$ with the fluctuating electric field gradient due to the solvent is shown on the basis of an upper limit estimate to be an inadequate mechanism.

On the basis of very crude estimates, it is likely that spin-orbit coupling enables the spins to feel the effects of modulation of the Stark splitting which quenches electronic orbital angular

momentum. However, it is not certain whether internal vibrations of the free radical ion or motions of the solvent molecules, or both, effect the modulation.

If the spin-orbit coupling is involved, an interesting possibility is that, for saturation experiments at least, statistical second order processes in contrast to the quantum mechanical second order processes of Van Vleck may be responsible for the observed relaxation.

Acknowledgements

Many stimulating and informative discussions with Professors H. Primakoff, S. I. Weissman, and J. Townsend are gratefully acknowledged. Without the chemical skill of Professor Weissman and his research group, the samples used would never have been available for these experiments.